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TECHNICAL NOTE

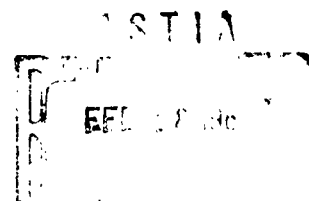
INVESTIGATION OF THE  $\pi$  ELECTRON SYSTEM  
OF URACIL WITH DIFFERENT SEMIEMPIRICAL METHODS

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For Research in Atomic, Molecular and Solid-State Theory  
Uppsala University, Uppsala, Sweden

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## ABSTRACT

The  $\pi$ -electron system of uracil was treated with the aid of the simple Hückel approximation, of the Hückel-CI method, of the semi-empirical SCF-LCAO-MO method and with the SCF-LCAO-MO-CI method. The excitation energies and oscillator strength values of the first four excited states were calculated. The calculations were performed with two different approximations for the form of the inter- $\pi$ -electronic repulsion integrals ( $r$ ).

The first excitation energy obtained with the aid of the Hückel-CI method gives good agreement with the experimental value in the case of one series of  $\gamma$  integrals. The SCF calculation in general has given worse results than the Hückel method taking into account the interaction of the  $\pi$  electrons and a limited CI (4 configurations) for the excited states. Since the interconfigurational matrix elements are very small, the CI has not a large influence on the results.

The conclusion was drawn that neither of the mentioned semi-empirical methods is suitable in its present form for the calculation of the spectra of heterocyclic molecules containing more than one heteroatom. The possibilities for the improvement of the methods are briefly mentioned.

## INTRODUCTION

Uracil (U) is one of the nucleotide bases occurring in RNA (ribonucleic acid). It differs from thymine (T) occurring in DNA (deoxyribonucleic acid) only by a methyl group (see Figure 1). Therefore, before investigating T, it seemed to be simpler to make an investigation on U, where the hyperconjugation of the methyl-group does not complicate the calculations

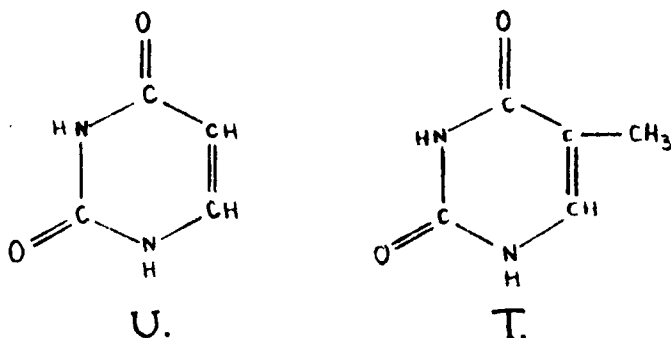


Fig. 1

It is well known that the semiempirical SCF-LCAO-MO method with limited CI for the excited states <sup>1, 2)</sup> has given quite good agreement with the experimental excitation energy and oscillation strength values for aromatic hydrocarbons <sup>1)</sup> and also for some heterocycles <sup>2, 3)</sup> containing N. Later it turned out that a simple Hückel type calculation with a limited CI for the excited states also gives good agreement with the experimental data for a large series of aromatic hydrocarbons <sup>4)</sup>.

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- 1) R. Pariser, and R.G. Parr, J. Chem. Phys. 21, 466 (1953);  
ibid. 21, 767 (1953).
  - 2) J.A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
  - 3) N. Mataga and K. Nishimoto, Z. physik. Chem. 13, 140 (1957).
  - 4) J. Koutecky, J. Paldus, R. Zahradník, J. Chem. Phys. (in the press.)
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There is, however, no experience with these simple semiempirical methods for heterocyclic molecules containing two different kinds of heteroatoms. The situation is further complicated by the fact that the two N atoms are in the  $sp^2$  hybrid state and so are giving two  $\pi$  electrons to the delocalized  $\pi$  electron system. To find an enough well working semiempirical method for such kinds of molecules as first step, we have made calculations on U in four approximations: 1) simple Hückel type calculation 2) Hückel calculation with limited CI for the first excited states 3) semiempirical SCF-LCAO-MO for the ground state and 4) semiempirical SCF-LCAO-MO with limited CI for the excited states. The aim of these calculations was to compare the excitation energy and oscillator strength values calculated with these different approximations with each other and with the experimental values. This comparison will perhaps give some insight how to change the original approximations of Pariser and Parr, resp. Pople, to be able to investigate such more complicated systems.

#### METHODS

- 1) The Hückel type calculation was performed neglecting overlap,

$$\Delta = 1, \quad (1)$$

determining the eigenvalues and eigenvectors of the matrix  $H$ ,

$$Hc = \epsilon c. \quad (2)$$

The used parameter values are given in Table I. The subscripts of the  $\alpha_c$

TABLE I. Parameter values used in the Hückel approximation of uracil.

$\alpha_c = 0$	$\alpha_{\substack{C \\ N \ O \ N}} = 0.34 \beta$	$\beta_{c,c} = \beta$
$\alpha_{\substack{C \\ N}} = 0.07 \beta$	$\alpha_{\substack{N \\ N}} = 0.90 \beta$	$\beta_{c,N} = 1.25 \beta$
$\alpha_{\substack{C \\ O}} = 0.20 \beta$	$\alpha_{\substack{O \\ N}} = 1.30 \beta$	$\beta_{c,O} = 1.50 \beta$
$\alpha_{\substack{C \\ N \ O}} = 0.27 \beta$		

parameters in the Table denote the  $\alpha$  value of a C atom which has as neighbours the atoms written in the subscript. The energy unit of the parameters equals according to Pariser and Parr <sup>1)</sup>,  $\beta = -2,39$  eV. The choice of the parameters is with some small changes the usual one as given in the literature (for details see reference 5).

The first excitation energy is given in this case by the energy difference of the lowest unfilled and highest filled MO

$$\Delta E = \epsilon_{m+1} - \epsilon_m, \quad (3)$$

where  $m$  denotes the highest filled level. The oscillator strength value is given by the formula

$$f = 1.085 \times 10^{-5} \nu R^2, \quad (4)$$

where  $\nu = \frac{\Delta E}{hc}$  is the wave number of the transition in  $\text{cm}^{-1}$  and  $R^2$ , the square of the transition moment should be substituted in  $\text{\AA}^2$ . The transition moment integral may be approximated again neglecting overlap with the expression <sup>6)</sup>

$$\underline{R} = \sqrt{2} \sum_{k=1}^n c_{m+1,k} c_{m,k} \underline{r}_k, \quad (5)$$

which is invariant to the choice of system of reference. Here  $n$  is the number of atoms giving  $\pi$  electrons to the system,  $\underline{r}_k$  denotes the position vector of the  $k$ -th atom and  $c_{m+1,k}$  resp.  $c_{m,k}$  its coefficients in the  $m+1$ -th, resp.  $m$ -th MO.

Having the eigenvectors  $\underline{c}_i$ , it is possible to calculate also the elements

$$p_{k,j}^{(0)} = 2 \sum_{l=1}^m c_{l,k} c_{l,j} \quad (6)$$

of the charge-bond order matrix  $\mathbf{p}^{(0)}$ , which are necessary for the further steps.

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5) T.A. Hoffmann and J. Ladik, to be published in *Advances in Chemical Physics*.

6) R. Daudel, R. Lefebvre and C. Moser, Quantum Chemistry, Interscience Publ. Inc., New York (1959).

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2) Hückel approximation with limited CI for the first excited states.

At this step we have solved the eigenvalue and eigenvector problem of the matrix  $F^{(1)}$ , which has the diagonal elements

$$F_{i,i}^{(1)} = -I_i + \frac{1}{2} P_{i,i}^{(0)} (I_i - E_i) + \sum_{j \neq i}^n (P_{j,j}^{(0)} - Z_j) \gamma_{i,j} \quad (7)$$

and the off-diagonal elements

$$F_{i,j}^{(1)} = \beta_{i,j} - \frac{1}{2} P_{i,j}^{(0)} \gamma_{i,j}. \quad (8)$$

The formulae are the same as those derived in Pople's paper <sup>2)</sup> ( $-I_i = U_{i,i}$ ,  $I_i - E_i = (ii|G|ii)$ ), but at this step we have used for the elements of the charge-bond order matrix  $P$  the elements  $P_{i,j}^{(0)}$  which we have obtained with the aid of the simple Hückel approximation (point 1). In formulae (7)-(8)  $I_i$  stands for the ionization potential and  $E_i$  for the electron affinity of atom  $i$ ,  $Z_j$  is the effective nuclear charge and  $\gamma_{i,j}$  is the Coulomb repulsion integral between a  $\pi$  electron belonging to atom  $i$  and another belonging to the atom  $j$ . In connection with formula (8) it should further be mentioned that here for the  $\beta_{i,j} = (\varphi_i | -\frac{1}{2} \Delta + V_{\text{core}} | \varphi_j)$  integrals only the  $\beta$ -s between the nearest neighbours were taken into account, but for the  $\gamma_{i,j}$  integrals also the interaction of  $\pi$  electrons not belonging to atoms which are nearest neighbours, should be considered <sup>1,2)</sup>. For  $\beta_{C,C} = \beta_{C,N}$  and  $\beta_{C,O}$  we have here used the same values as in the simple Hückel approximation (see Table I).

For the  $\gamma_{i,j}$  integrals we have used in one set of calculations the expression given by Mataga and Nishimoto <sup>3)</sup>,

$$\gamma_i = \gamma_{i,j} = e^2 / (a_{i,j} + R_{i,j}), \quad (9)$$

where  $R_{i,j}$  <sup>7)</sup> is the internuclear distance and the constant  $a_{i,j}$  was determined for the case when the atoms  $i$  and  $j$  are of the same kind, from the equation

$$\gamma_{i,i} = e^2 / a_{i,i} = I_i - E_i, \quad (10)$$

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7) The geometrical data necessary for the calculation were taken from the paper: M. Spencer, Acta Cryst. 12, 59 (1959).

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and for the case, when the atoms  $i$  and  $j$  are of different kinds, from the equation

$$e^2/a_{i,j} = \frac{1}{2}[I_i - E_i + I_j - E_j]. \quad (11)$$

In another set of calculations we have for these integrals used the expression

$$\gamma_2 = \gamma_{i,j} = e^2/(a_{i,j}^2 + R_{i,j}^2)^{1/2} \quad (12)$$

advised to be a better approximation <sup>8)</sup> with the same constants  $a_{i,j}$  as in expression (9).

For the ionization potentials and electron affinities we have used in the cases of C and O atoms the values given by Pritchard and Skinner <sup>9)</sup>. For the N atom, however, taking into account that in uracil both N-atoms are in the  $sp^2$  hybrid state and are giving therefore 2  $\pi$ -electrons to the  $\pi$  electron system, we have used the ionization potential value of an  $N^+$  ion, which was estimated in the appropriate valence state to be 29.16 eV <sup>8)</sup>. For similar reasons the electron affinities of these N-atoms were taken equal to the electron affinity of an  $N^+$  ion, i.e. with the ionization potential of an N-atom ( $E_{N^+} = I_N$ ). For the effective nuclear charge we have used the approximate values  $Z_C = Z_O = 1$  for the C and O atoms and  $Z_N = 2$  for the N atoms.

Having solved the eigenvalue problem

$$F^{(1)} C_t^{(1)} = \epsilon_t C_t^{(1)}, \quad (13)$$

we have taken into account for the first excited states a limited CI including only the first four excitations,  $m \rightarrow m+1$ ,  $m \rightarrow m+2$ ,  $m-1 \rightarrow m+1$  and  $m-1 \rightarrow m+2$ , where  $m$  denotes the quantum number of the highest filled MO (in uracil we have 10  $\pi$  electrons, therefore  $m = 5$ ). In the case of singlet-singlet transition the inter-configurational matrix element between the transitions  $i \rightarrow j$  and  $k \rightarrow l$ , as can be readily shown (see eq. (14) of reference 3 and take into account the neglect of differential overlap),

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<sup>8)</sup> K. Ohno, personal communication.

<sup>9)</sup> H.O. Pritchard and H.A. Skinner, Chem. Revs. 55, 745 (1955).

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has the general form

$${}^1G_{i \rightarrow k}^{j \rightarrow l} \equiv ({}^1\Phi_{i \rightarrow k} | H | {}^1\Phi_{j \rightarrow l}) =$$

$$= \sum_{p=1}^8 \sum_{r=1}^8 (2c_{lp}c_{jp}c_{kr}c_{ir} - c_{ip}c_{jp}c_{kr}c_{lr}) \gamma_{pr} + (\epsilon_k - \epsilon_i) \delta_{ij} \delta_{kl} . \quad (14)$$

Here  $n$  is the number of centers (in uracil  $n = 8$ ), the  $c_{l,p} \dots$  constants denote the appropriate components of the eigenvectors  $(i, k, \text{resp. } j, l)$  involved in the matrix element  ${}^1G_{i \rightarrow k}^{j \rightarrow l}$  and  $\delta_{i,j}$  and  $\delta_{k,l}$  are Kronecker  $\delta$ -s. In the case of uracil with the limited CI mentioned above we have  $i = 4, 5, j = 4, 5, k = 6, 7, \text{and } l = 6, 7$ . In the case of a singlet-triplet transition we have an expression which differs from (14) only by not containing the first (exchange) term in the parenthesis.

It should be mentioned further that for the off-diagonal elements of the matrix  $\mathbf{G}$  the expression is only then valid when  $i \neq j$  and simultaneously  $l \neq k$ . In the case when  $i = j$  and  $k \neq l$  or  $i \neq j$ , but  $k = l$  there will be a contribution also from the one-electron part of the Hamiltonian. In the cases of aromatic hydrocarbons, they are, however, equal to zero in consequence of the molecular symmetry, and also in the non-zero cases they are small compared with the terms occurring in (14)<sup>4</sup>. In the case of uracil this situation is perhaps changed in consequence of the heteroatoms, but as first approximations to avoid very complex calculations we have neglected these terms. In a more accurate calculation, however, this point should be investigated thoroughly.

Solving the eigenvalue problem of the matrix  $\mathbf{G}$  with elements given by (14)

$$\mathbf{G} \mathbf{b}_v = E_v \mathbf{b}_v, \quad v = 1, 2, 3, 4, \quad (15)$$

we get as eigenvalues directly the excitation energies of uracil with the mentioned limited CI. (Since we have taken into account only four excitations, the matrix  $\mathbf{G}$  will have the order of 4 and we get the first four excitation energies of uracil).

Having the eigenvectors  $\mathbf{b}_v$  it is easy to calculate the oscillator strength values of the first four excitations again with the aid of Eq. (4), but now to each excited state corresponds a different  $v$  value,

$$\nu_v = \frac{E_v}{hc} \quad \text{and a different } \underline{R} \text{ vector,}$$

$$\underline{R}_v = \sum_{\substack{i=4,5 \\ k=6,7}} b_{v,i \rightarrow k} \underline{R}_{i \rightarrow k}, \quad (16)$$

$$f_v = 1.085 \times 10^{-5} \nu_v R_v^2, \quad v = 1, 2, 3, 4. \quad (17)$$

Here the transition moment integrals  $R_{i \rightarrow k}$  can be calculated again with the aid of Eq. (5):

$$R_{i \rightarrow k} = \sqrt{2} \sum_{p=1}^n c_{kp} c_{ip} \Gamma_p, \quad (18)$$

$i = 4, 5; \quad k = 6, 7.$

### 3) Semi-empirical SCF-LCAO-MO approximation.

At this approximation again the matrix  $\mathbf{F}$  was used with elements (7) and (8) and with the same constant as mentioned in point 2), but after each iteration step the charge-bond order matrix was formed with the obtained eigenvectors and substituted into (7) and (8) until self-consistency. The first singlet excitation energy is at this approximation the first diagonal element of the matrix  $\mathbf{G}$  with the SCF eigenvalues and eigenvectors

$$\begin{aligned} {}^1\Delta E &= ({}^1G_{5 \rightarrow 6}^{5 \rightarrow 6})_{SCF} = \\ &= \sum_{p=1}^8 \sum_{r=1}^8 (2 c_{6p}^{SCF} c_{5p}^{SCF} c_{6r}^{SCF} c_{5r}^{SCF} - (c_{5p}^{SCF} c_{6r}^{SCF})^2) \gamma_{pr} + \epsilon_6^{SCF} - \epsilon_5^{SCF}, \end{aligned} \quad (19)$$

and for the calculation of the oscillator strength equations (4) and (5) were used with the appropriate SCF eigenvector components and with  ${}^1\Delta E$  given by (19).

### 4) Semi-empirical SCF-LCAO-MO with limited CI for the first excited states.

At this final step the same formalism was used as in point 2) with the same constants in the elements of the  $\mathbf{F}$  matrix, but everywhere the SCF eigenvalues and eigenvectors were substituted in the equations.

## RESULTS

In Table II the excitation energies of uracil calculated in the four different approximations are given in  $\beta$  units ( $\beta = -2.39$  eV).

TABLE II Excitation energies of uracil.

	Hückel	Hückel-CI		SCF		SCF-CI		Exp.
		$\gamma_1$	$\gamma_2$	$\gamma_1$	$\gamma_2$	$\gamma_1$	$\gamma_2$	
$^1\Delta E_1$	-1.628	-1.955	-1.813	-2.395	-2.321	-2.374	-2.312 (-2.316)	-1.995
$^3\Delta E_1$				-1.020	-1.319			
$^1\Delta E_2$		-2.314	-2.468			-2.816	-3.169 (-3.177)	> -2.470
$^1\Delta E_3$		-2.558	-2.752			-2.994	-3.219 (-3.221)	
$^1\Delta E_4$		-3.189	-3.094			-3.645	-3.665	

In the Table  $\Delta E_i$  denotes the excitation energy of the  $i$ -th excited state, the CI taken into account.  $\gamma_1$  and  $\gamma_2$  stand for the two different approximate expressions of the inter  $\pi$  electronic repulsion integrals (see Eq. (9), resp. Eq. (12)). The experimental value of  $^1\Delta E_1$  refers to the first absorption maximum of uracil <sup>10)</sup> (260 m $\mu$ ) and the inequality for the experimental value of  $^1\Delta E_2$  is taken from the same curve ( $\lambda_{\max, 2} < 210$  m $\mu$ ). The figures in parentheses in column SCF-CI  $\gamma_2$  indicate the results of a calculation, which has taken into account three excited configurations instead of four.

<sup>10)</sup> G.H. Beaven, E.R. Holiday, and E.A. Johnson in the Nucleic Acids, Ed. E. Chargaff and I.N. Davidson, Vol. I., Academic Press, New York (1955), p. 493.

Figure 2 denote the  $\pi$  electron charge densities and bond orders of uracil in the simple Hückel approximation (a) and in the semi-empirical SCF-LCAO-MO approximation using the two different sets of  $\gamma$  integrals (b) and (c).

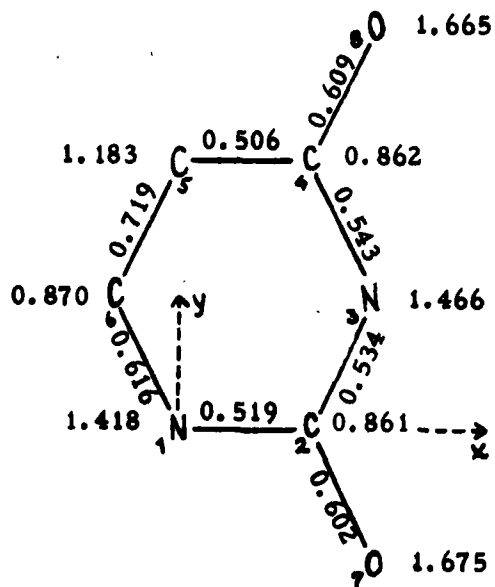


Fig. 2 (a) Hückel

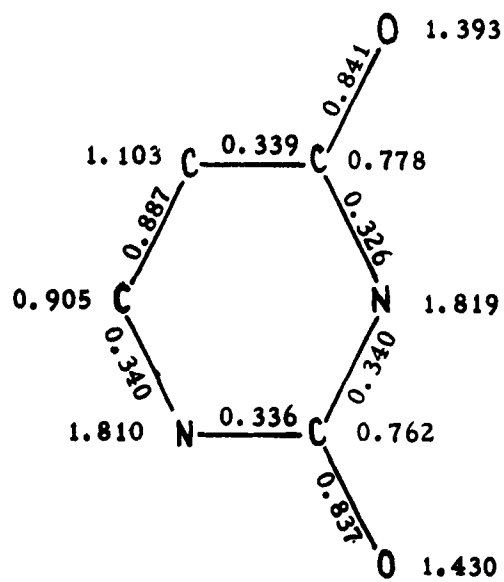


Fig. 2 (b) SCF- $\gamma_1$

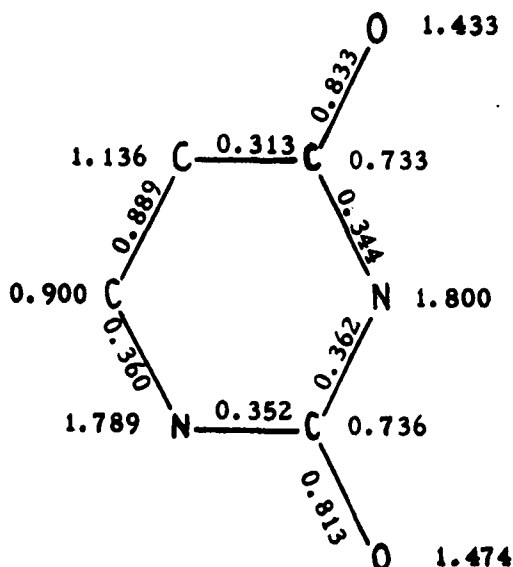


Fig. 2 (c) SCF- $\gamma_2$

In Table III the oscillator strength values of the different transitions are given together with the transition moment vectors of the first transition.

TABLE III Oscillator strength values and the transition moment vector of the first transition of uracil.

	Hückel	Hückel - CI		SCF		SCF - CI		Exp
		$\gamma_1$	$\gamma_2$	$\gamma_1$	$\gamma_2$	$\gamma_1$	$\gamma_2$	
$f_1$	0.492	0.602	0.492	0.816	0.723	0.680	0.653 (0.075)	$\approx 0.25$
$f_2$		0.006	0.083			0.118	0.129 (0.075)	
$f_3$		0.228	0.291			0.207	0.202 (0.429)	
$f_4$		0.811	0.779			0.835	0.759	
$R_1$	1.208	1.219	1.144	1.283	1.231	1.176	1.168	
$\varphi_1$	$76,8^\circ$	$59,8^\circ$	$64,8^\circ$	$60,6^\circ$	$64.2^\circ$	$57,8^\circ$	$64.3^\circ$	

In the Table  $f_i$  denotes the oscillator strength value of the  $i$ -th singlet-singlet excitation,  $R_1$  the absolute value of the transition moment vector of the first excitation in Å units and the angle  $\varphi_1$  is the angle between its direction and the  $x$  axis which is directed from N atom 1 towards C atom 2 (see Figure 2a). In the case of SCF-CI  $\gamma_2$  the values in parentheses refer again to the 3 configuration calculation, but the  $R_1$  and  $\varphi_1$  values given in this column refer to the 4 configuration case. The experimental value of  $f_1$  was estimated by Tinoco <sup>11)</sup> to be 0.21 for the case of thymine. Since the absorption of uracil is a little more intensive, the value  $f_1 \approx 0.25$  seems to be a reasonable one.

<sup>11)</sup> I. Tinoco, Jr., J. Am. Chem. Soc. 82, 4785 (1960).

## DISCUSSION

Comparing the first singlet excitation energy calculated with different methods with the experimental value it can be seen that the best agreement is in the case of the Hückel-CI method using the first series of  $\gamma$  integrals ( $\gamma_1$ ) [ ${}^1\Delta E_{1,\text{theor}} = -1.955 \beta$ ,  ${}^1\Delta E_{1,\text{exp}} = -1.995 \beta$ ]. It is interesting to point out that the SCF method without and with CI gives a much worse agreement than the Hückel method after one iteration process taking into account also the inter  $\pi$ -electronic repulsion and a limited CI for the excited state. The reason for this is probably that the closed shell form of SCF-LCAO-MO used here is not applicable to the excited states. Only a closed shell SCF calculation for the ground state and an open shell calculation for the excited state would probably give good results for the excitation energies. Further it should be mentioned that the very little change of  ${}^1\Delta E_1$  in consequence of the CI (compare column SCF and SCF-CI). This is in agreement with the fact that interconfiguration matrix elements obtained are very small. This is the situation also in the case of the Hückel-CI calculation. The smallness of the interconfigurational matrix elements is probably the consequence of the two O atom substituents on the ring, which spoil the symmetry of the pyrimidine ring. In connection with the interconfigurational matrix elements, it should further be mentioned that since they are very small, the neglect of their parts coming from the matrix element of the one-electron Hamiltonian if  $i = j$  and  $k \neq l$ , or  $i \neq j$  and  $k = l$ , is not justified. In a more accurate calculation for heterocyclic molecules, these contributions to the interconfigurational matrix elements should be taken into account.

The excitation energy of the second singlet excited state ( ${}^1\Delta E_2$ ) is not measured experimentally, but its value may be estimated from the rising absorption curve to the  ${}^1\Delta E_2 \approx 2.5 - 2.6 \beta$ . This value is again in enough good agreement with the result of the Hückel-CI method, but with the second series of  $\gamma$  integrals ( $\gamma_2$ ) applied. Assuming the large energy difference  ${}^1\Delta E_2 - {}^1\Delta E_1 = 0.55 \beta$  on the basis of the estimated value of  ${}^1\Delta E_2 = 2.55 \beta$  it is interesting to compare this figure with the theoretical values. These are the following: Hückel-CI ( $\gamma_1$ ) =  $0.35 \beta$ ; Hückel-CI ( $\gamma_2$ ) =  $0.66 \beta$ ; SCF-CI ( $\gamma_1$ ) =  $0.55 \beta$ ; SCF-CI ( $\gamma_2$ ) =  $0.86 \beta$ . It can be seen that in this case, the SCF-CI method with the  $\gamma_1$  integrals gives the best agreement.



We have also performed the SCF-CI calculation taking into account only the three  $5 \rightarrow 6$ ,  $5 \rightarrow 7$ ,  $4 \rightarrow 6$  excited configurations with the  $\gamma_2$  series of integrals. The excitation energies obtained indicate that there is a very little change as compared to the 4 excited configurational case.

Comparing the molecular diagrams of the ground state of uracil shown in Figure 2, it can be seen that the simple Hückel approximation (Fig. 2a) has given too low charge densities on the hybridised N atoms and too high ones on the oxygen atoms, whereas in the case of the SCF calculation we have got more reliable values for these charge densities. Further it is apparent that for the two different approximations of the  $\gamma$  integrals in the SCF method, we get only slightly different electronic distribution. (Fig. 2b and 2c).

The calculated oscillator strength values shown in Table III are in enough bad agreement with the experimental value of  $\approx 0.25$ . The relatively best agreement is achieved in the simple Hückel case and in the case of Hückel-CI with  $\gamma_2$  (in both cases for the first excitation  $f_1 = 0.492$ ). It should be mentioned that the CI has a much larger influence on  $f_1$  than on the excitation energies (compare the figures given in the first row of Table III). In connection with the f-values of the higher excited states it should be mentioned that the calculated  $f_2$  and  $f_3$  values are in all cases much lower than the appropriate  $f_1$  values, whereas the experimental curve shows a higher intensity for the second excitation than for the first one<sup>10</sup>). It would be very useful to have a detailed band assignment for uracil to be able to compare successfully the theoretical and experimental excitation energies and f values. At the same time it should be emphasized that a limited CI calculation gives in most cases somewhat reliable results for the first excited state, but not for the higher ones.

The transition moment vectors of the first excitation indicated in the last two rows of Table III show that this vector is directed approximately from N-atom 1 towards C-atom 4 ( $\varphi_{1,av} \approx 60^\circ$ , when we do not take into account the result of the simple Hückel calculation of  $77^\circ$ ) and its length is  $R_{1,av} \approx 1.20 \text{ \AA}$ ).

In connection with the two different sets of  $\gamma_{i,j}$  integrals used during the calculation it should be mentioned that in some cases the series  $\gamma_1$ , in other cases the series  $\gamma_2$  has given better agreement with the experiment and therefore on the basis of these results it is not possible to make a decision about their applicability.

Summarizing the conclusions it seems so that neither of the applied four semiempirical methods gives a satisfactory explanation of the spectrum of uracil. In order to compare the semi-empirical methods, which were used in their original form given in the literature <sup>1-4)</sup>, they should be improved to describe correctly the electronic structure of molecules with more than one kind of heteroatoms. The improvements will probably be possible to achieve by

- 1) taking into account the variation of the effective nuclear charge of the ionization potential and electron affinity with the  $\pi$  electron density of the atoms,
- 2) detailed investigation of the  $F_{i,i}$  matrix elements (Eq. 7) of atoms contributing two  $\pi$  electrons to the delocalized  $\pi$  electron system,
- 3) the consideration of the parts of the interconfigurational matrix elements arising from the one electron part of the Hamiltonian,
- 4) taking into account more configurations for the excited state to be able to describe also the higher excited states,
- 5) systematic investigation of the influence of the different approximations of the  $\gamma_{i,j}$  integrals and the variation of the  $\beta_{i,j}$  integrals (see Eq. 8).

These calculations should be performed on a series of similar molecules to have larger material for comparison and to avoid wrong conclusions in consequence of possible coincidence of theoretical and experimental data by accident.

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